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Method for regeneration of an electrolysis bath for the
production of a compound I-III-VI₂ in thin layers

The present invention relates to the production of
5 semiconductors of the I-III-VI₂ type in thin film form,
especially for the design of solar cells.

I-III-VI₂ compounds of the CuIn_xGa_(1-x)Se_yS_(2-y) type
(where x is substantially between 0 and 1 and y is
10 substantially between 0 and 2) are regarded as very
promising and could constitute the next generation of
thin-film photovoltaic cells. These compounds have a
wide direct bandgap of between 1.05 and 1.6 eV, which
allows solar radiation in the visible to be strongly
15 absorbed.

Record photovoltaic conversion efficiencies have been
achieved by preparing thin films by evaporation on
small areas. However, evaporation is difficult to adapt
20 to the industrial scale because of problems of
nonuniformity and low utilization of raw materials.
Sputtering is better suited to large areas, but it
requires very expensive vacuum equipment and precursor
targets.

25 There is therefore a real need for alternative, low-
cost atmospheric-pressure, techniques. The technique of
thin-film deposition by electrochemistry, in particular
by electrolysis, appears to be a very attractive
30 alternative. The advantages of this deposition
technique are numerous, and in particular the
following:

- deposition at ambient temperature and ambient
pressure in an electrolysis bath;
- 35 - possibility of handling large areas with high
uniformity;
- ease of implementation;
- low installation and raw material costs (no

special forming operation, high level of material utilization); and

- great variety of possible deposit shapes due to the localized nature of the deposit on the substrate.

5

Despite extensive research in this field, the difficulties encountered relate to the control of the quality of the electrodeposited precursors (composition and morphology) and the efficiency of the electrolysis bath after several successive depositions.

It is an object of the present invention to propose a method of producing thin films of a I-III-VI_y compound (where y is close to 2) by electrolysis, which ensures that the deposition conditions are stable and reproducible.

A further object is to be able to carry out, over large areas, a large number of successive depositions of thin films having the desired morphology and the desired composition.

Another object of the present invention is to propose a method of producing thin films of the I-III-VI_y compound, which ensures a satisfactory lifetime of the electrolysis bath and effective regeneration of the raw materials consumed during the electrolysis.

Another object of the present invention is to propose a method of producing thin films of the I-III-VI_y compound, which ensures that the raw materials consumed during the electrolysis are regenerated, without in any way causing the composition of the electrolysis bath to go out of equilibrium and therefore reducing its lifetime.

For this purpose, the subject of the invention is a method of producing a I-III-VI_y compound in thin film form by electrochemistry, in which y is close to 2 and

VI is an element comprising selenium, of the type comprising the following steps:

5 a) of providing an electrolysis bath comprising active selenium, in oxidation state IV, and at least two electrodes; and

b) of applying a potential difference between the two electrodes in order to substantially promote migration of the active selenium toward one of the electrodes and thus initiate the formation of at least
10 one thin film of I-III-VI_y.

Within the context of the invention, the method furthermore includes a step c) of regenerating the selenium in active form in said bath, in order to
15 increase the lifetime of said electrolysis bath.

Thus, within the context of the present invention, the method begins by regenerating the bath in terms of active selenium before regenerating it in terms of
20 element I (such as copper) and/or element III (such as indium or gallium). This is because it has been found that a slight reintroduction of active selenium in the bath (preferably an excess of about 20% in molar concentration relative to the amount of selenium
25 normally added) makes it possible again to obtain substantially the same number and the same volume of thin films as those obtained after step b).

Advantageously, after step c), at least one new thin
30 film of I-III-VI_y is formed.

Thus, in a first embodiment, at step c), selenium is added to the bath in order to form an excess of active selenium in the bath.

35

In another embodiment, as a variant of or in addition to the aforementioned first embodiment, at step c), an oxidizing agent for selenium is introduced into the bath in order to regenerate selenium in active form.

Usually, the electrolysis bath, when it ages over the course of the deposition, has selenium colloids. This selenium in colloid form is in oxidation state 0 and, within the context of the present invention, is not capable of combining with the elements I and III.

Advantageously, if the bath contains selenium in colloid form at step b), the aforementioned oxidizing agent is capable of regenerating the selenium in colloid form to selenium in active form.

Thus, it will be understood that the expression "selenium in active form" means selenium in oxidation state IV, which is capable of being reduced at the electrode to the ionic form SE^{2-} and of combining naturally with the elements I and III in order to form the thin films of I-III- VI_y , and being distinguished from selenium in oxidation state 0, for example in the form of colloids in the solution of the bath, which does not combine with the elements I and III.

In a particularly advantageous embodiment, said oxidizing agent is hydrogen peroxide, preferably with a concentration in the bath of the order of magnitude corresponding substantially to at least five times the initial selenium concentration in the bath.

The addition of hydrogen peroxide to the bath therefore makes it possible to regenerate the electrolysis bath at very low cost. In addition, this regeneration is carried out without contaminating the bath since a simple degassing operation allows the initial constitution of the bath to be recovered.

In this regard, in which the electrolysis bath is regenerated by limiting its contamination by the regenerating additives, it is advantageous to provide a step after step c), of regenerating the electrolysis

bath by introducing oxides and/or hydroxides of elements I and III.

Other advantages and features of the invention will
5 become apparent on reading the detailed description
below of embodiments given by way of nonlimiting
examples, and by examining the drawings which accompany
it, in which:

- figure 1 shows schematically a thin film
10 obtained by implementing the method according to the
invention; and

- figure 2 shows schematically an electrolysis
bath for implementing the method according to the
invention.

15 Referring to figure 1, copper indium diselenide films
CO are obtained at room pressure and room temperature
by electrodeposition of a thin precursor film of
suitable composition and suitable morphology on a glass
20 substrate S coated with molybdenum Mo. The term
"precursor film" is understood to mean a thin layer of
overall composition close to CuInSe_2 and obtained
directly after deposition by electrolysis, without any
subsequent treatment.

25 The electrodeposition is carried out using an acid bath
B (figure 2), stirred by blades M, which contains an
indium salt, a copper salt and selenium oxide in
solution. The concentrations of these precursor
30 elements are between 10^{-4} and 10^{-2} M. The pH of the
solution is set between 1 and 4.

Three electrodes, An, Ca and REF, including:

- a molybdenum electrode Ca (standing for
35 cathode) on which the thin film forms by
electrodeposition; and

- a mercurous sulfate reference electrode REF,
are immersed in the bath B.

The electrical potential difference applied to the molybdenum electrode is between -0.8 and -1.2 V relative to the reference electrode REF.

- 5 Layers having a thickness of between 1 and 4 microns are obtained with current densities of between 0.5 and 10 mA/cm².

10 Under the defined composition, stirring and potential difference conditions, it is possible to obtain dense adherent films of homogeneous morphology, the composition of which is close to the stoichiometric composition: Cu (25%); In (25 + ε%) and Se (50%), with
15 a composition slightly richer in indium, as Table I below shows. It is thus possible to deposit films on areas of 10 × 10 cm².

An exemplary embodiment of the invention is given below.

20

A typical deposit was produced from a bath whose initial formulation was the following:

- [CuSO₄] = 1.0 × 10⁻³ M;
[In₂(SO₄)₃] = 3.0 × 10⁻³ M;
25 [H₂SeO₃] = 1.7 × 7.10⁻³ M;
[Na₂SO₄] = 0.1 M,

where the notation "M" corresponds to the unit "mole per liter", for a pH of 2.2.

30

The precursors were deposited by a cathodic reaction for a set potential of -1 V relative to the electrode REF. The current density was -1 mA/cm².

- 35 After each electrolysis, the bath was recharged with elements Cu, In and Se on the basis of the number of coulombs indicated by a detection cell (not shown) which thus counts the number of ions that are interacted with the solution of the bath. This

recharging allowed the concentration of the elements to be kept constant over the course of the successive electrodeposition operations. The pH could also be readjusted by adding sodium hydroxide (such as NaOH, for a concentration such as 1 M), but this measure is not systematically necessary here, as will be seen later.

Under these conditions, it was usually found that, after an indication of 500 ± 100 coulombs in a 1-liter solution (corresponding to the electrodeposition of 4 to 5 thin films of 25 cm^2 area with a thickness of $2 \text{ }\mu\text{m}$), partial or complete debonding of the CuInSe_2 films systematically occurs.

According to the invention, this debonding disappeared by regenerating the bath with selenium, before even regenerating the elements Cu and In.

A distinction should be made here between active selenium of oxidation state IV, usually denoted Se(IV) , and inactive selenium, in oxidation state 0, which is generally observed in the form of colloids in the electrolysis bath and usually denoted by Se(0) .

It should be pointed out that it is only active selenium Se(IV) that is capable of being reduced at the electrode Ca to the ionic form Se^{2-} and of being combined, in this form, with the elements Cu and In to form the thin films of CuInSe_2 .

It should also be pointed out that there are two competitive reactions during the electrolysis: the selenium introduced into the bath can be converted at the electrode:

- either into Se^{2-} favorable to the formation of the thin films as indicated above;

- or to Se(0) in colloid form, which is not favorable to the formation of thin films, especially

because the colloids pose problems at the interface between the substrate (or the molybdenum layer MO here) and the thin Cu-In-Se film being formed.

5 Advantageously, regeneration is carried out with an excess of Se(IV) in the bath. For this purpose, selenium oxide is added, dissolved in the electrolysis bath, in order to slow down the ageing of the bath. In practice, for a thin film formed and 115 coulombs
10 passing through the solution, it is theoretically necessary to add 1.8×10^{-4} M of $[\text{H}_2\text{SeO}_3]$ to the solution in order to have an initial selenium concentration of 1.7×10^{-3} M again. An addition of twice this amount (i.e. 3.6×10^{-4} M and therefore an excess of
15 1.8×10^{-4} M of $[\text{H}_2\text{SeO}_3]$), at the fifth deposition, makes it possible to obtain adherent films again. These thin films have the desired morphology and the desired composition (Table I). An over-regeneration of 3.6×10^{-4} M thus makes it possible to obtain a cycle of
20 4 to 5 films of satisfactory adhesion before further debonding problems are observed. After each debonding cycle, the renewal of this operation allows adherent films to be obtained.

25 As a variant of or in addition to this operation, an oxidizing agent for reoxidizing the selenium in Se(0) form is used in order to obtain selenium in Se(IV) form. For this purpose, it is preferred to use hydrogen peroxide H_2O_2 , employing H_2O_2 in large excess in the
30 solution (concentration of the order of 10^{-2} M, preferably close to 4×10^{-2} M). The films become adherent again for 4 to 5 successive thin-film deposition operations, before they become debonded again. The renewal of this operation also makes it
35 possible to obtain adherent films again. Advantageously, it has been observed that the addition of hydrogen peroxide furthermore makes it possible to obtain thin films of relatively smoother morphology.

Thus, it has been found that there is a great similarity between the effects provided by Se(IV) over-regeneration and H_2O_2 addition to the solution. It may also be pointed out that other types of oxidizing agent
5 than hydrogen peroxide, especially ozone O_3 , may be used in order to increase the lifetime of the baths.

The composition (Table I) and the morphology of the films are substantially the same as when hydrogen
10 peroxide was added to the bath or when selenium (IV) was regenerated.

Table I: Comparative analysis of the composition of the thin electrodeposited $CuInSe_2$ films as a function of
15 excess selenium Se(IV) over-regeneration and addition of hydrogen peroxide.

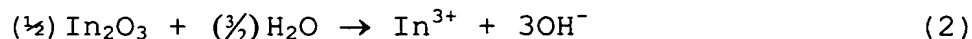
	Cu (%)	In (%)	Se (%)
First deposit	21.4	27.5	51
Addition of H_2O_2	22.9	25	52
Excess regeneration of Se(IV)	21.4	28.8	49.7

The addition of hydrogen peroxide or the excess
20 regeneration of Se(IV) makes it possible to considerably increase the number of films that can be deposited with one bath. Such recycling of the bath makes it possible for the elements introduced, and more particularly the indium, to be entirely consumed by
25 electrolysis. This makes it possible, particularly advantageously, to reduce the precursor production costs, especially compared with evaporation or sputtering methods.

30 It should be pointed out that, according to an advantageous aspect of the regeneration of the bath within the context of the invention, copper and/or indium oxides or hydroxides are also added in order to regenerate the $CuInSe_2$ electrolysis bath in terms of

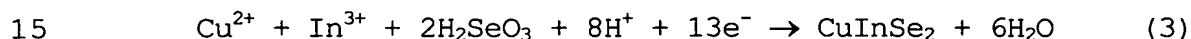
copper and/or indium.

For example, by adding copper oxide CuO and indium oxide In₂O₃ to the bath, the following reactions (1) and (2) occur:

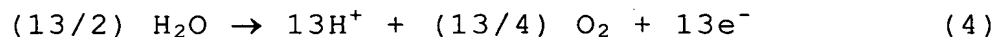


In contrast, if the compounds CuSO₄ and In₂(SO₄)₃ have been added, the bath would have been contaminated with SO₄²⁻ sulfate ions.

Furthermore, the reaction to form CuInSe₂ at the cathode is written as:



where e⁻ corresponds to an electron, whereas at the anode, the following reaction takes place:



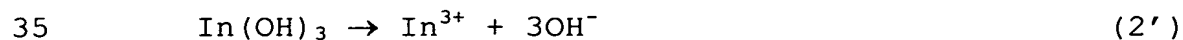
in order to maintain charge equilibrium.

20

According to another advantage provided by the addition of Cu and In oxides, it has been found that the difference of five H⁺ ions in excess between equations (3) and (4) is compensated for by the five OH⁻ ions introduced by the reactions (1) and (2). Thus it will be understood that the addition of Cu and In oxides furthermore makes it possible to stabilize the pH of the solution and to dispense with the addition of sodium hydroxide as mentioned above.

30

It may furthermore be pointed out that the addition of hydroxides Cu(OH)₂ and In(OH)₃ produces the same effects, the reactions (1) and (2) becoming simply:



Thus, the longevity and stability of the baths for electrodepositing I-III-VI_y compounds such as Cu-In-Se_y (with y close to 2) are ensured by the addition of agents that do not affect the quality of the films. The

electrodeposited precursor film contains the elements in a composition close to I-III-VI₂ stoichiometry. The compositions and the morphology are controlled during the electrolysis. These agents (excess Se(IV) or H₂O₂) may be readily used for any type of electrolysis bath for electrodepositing I-III-VI systems such as Cu-In-Ga-Al-Se-S.

The conversion efficiencies obtained (9% without a surface antireflection film) attest to the quality of the deposits obtained by the method according to the invention.

Of course, the present invention is not limited to the embodiment described above by way of example; rather it extends to other alternative embodiments.

Thus, it will be understood that the elements I and III initially introduced into the solution in CuSO₄ and In₂(SO₄)₃ form may advantageously be introduced rather in the form of copper and indium oxides or hydroxides in order to limit contamination of the bath.